CHAPTER I
INTRODUCTION

Reppe and Schweckendiek (154) discovered the catalytic action of phosphine complexes of metal halides and metal carbonyls in the cyclization of olefins, acetylene and their derivatives. This seems to have stimulated interest in the chemistry of the complexes of tertiary phosphines and arsines with metal ions, though the foundation of this field was laid nearly a century back by Hofmann (106) who prepared complexes of gold and platinum with triethylphosphate. Some of the factors which have contributed towards this tremendous interest in this field of phosphines and their metal complexes, may be briefly illustrated with the help of following examples.

Some novel features of tertiary phosphines as ligands

Certain tertiary phosphines are known to form complexes with metal halides in which the metal has higher coordination number than that with other ligands and consequently an unusual stereochemistry. Lewis and Whyman (120) have prepared seven coordinate molybdenum(II) and tungsten(II) complexes $[M(CO)_3(DPE)X_2]$ ($X$ is Br or I) by the treatment of the corresponding metal-tetracarbonyl diphosphine complex, $[M(CO)_4(diphos.)]$, with two equivalents of bromine or iodine in methylene dichloride. These complexes were assumed to have
pentagonal bipyramidal configuration by analogy with the corresponding diarsine complexes prepared by Nyholm and his coworkers (144). Venanzi and his coworkers (92) have reported the formation of five coordinate palladium(II) and platinum(II) complexes of the type $[MX(QP)]X'$ (where $QP$ is tris(o-diphenylphosphinophenyl)phosphine and $X$ is halogen). Because of the similarity in physical properties of these complexes and of those formed by the corresponding arsine, they have been assigned trigonal bipyramidal configuration.

The tertiary phosphines, particularly the ditertiary phosphines, have been used for the stabilization of a number of hydrido complexes of transition metals. Chatt and his coworkers (33) have prepared a very stable chlorohydride of platinum $([\text{PET}_3]_2\text{PtHCl})$ by the reduction of cis- or trans- $([\text{PET}_3]_2\text{PtCl}_2)$. This was the first example of a transition metal hydride existing in discreet molecules and without carbon as a ligand atom. Similarly Chatt and Hayter (41) have obtained octahedral hydrido complexes trans-$[\text{MX}(\text{diphos.})_2]$ (M is Ru and Os; diphos is $\sigma$-$\text{C}_6\text{H}_4(\text{PET}_{2})_2$, $\text{CH}_2\{\text{P}(\text{C}_6\text{H}_5)\}_2$ and $\text{C}_2\text{H}_4(\text{PET}_{2})_2$ (where $R = \text{CH}_3$ or $\text{C}_2\text{H}_5$) by the reduction of the corresponding ruthenium(II) or osmium(II) cis-isomer with lithium aluminium hydride. On further treatment with lithium aluminium hydride, the complexes trans-$[\text{RuHCl}(\text{diphos})_2]$ gave the corresponding dihydride trans-$[\text{RuH}_2(\text{diphos})_2]$; diphos is $\text{C}_2\text{H}_4(\text{PET}_{2})_2$ and $\sigma$-$\text{C}_6\text{H}_4(\text{PET}_{2})_2$. 
The alkyl and aryl derivatives of transition metals have been prepared through their stabilization by phosphines. Chatt and Shaw (49) have prepared stable aryls of cobalt(II) and iron(II) of the type trans \[\text{MR}_2\left(\text{Et}_2\text{PhP}\right)_2\] (R is ortho substituted aryl group) by the reaction of Grignard reagent with the tertiary phosphine-metal halide complex. Chatt and Shaw (47) have also prepared alkyl platinum complexes of the type trans- \[(\text{PR}_3)_2\text{PtMeX}\] and cis- \[(\text{PR}_3)_2\text{PtMe}_2\] by the action of methyl lithium or methyl magnesium halide on cis- or trans \[(\text{R}_3\text{P})_2\text{PtX}_2\]; (R is Et, Pr or Ph; X is Cl, Br or I).

In case of several transition metals, a number of oxidation states for each metal have been stabilized by the use of tertiary phosphines as ligands. Chatt and Hart (34) have prepared the zerovalent nickel complex \[\text{Ni(CO)}_2\text{(diphos)}\] by reacting tetracarbonylnickel (0) with 1,2-bis(diethylphosphino)ethane. With 1,2-bis(diphenylphosphino)ethane they obtained the zerovalent complex \[\text{Ni(diphos)}_2\]. Porri and his coworkers (151) have reported the preparation of nickel(I) complex \[\text{NiX(Ph}_3\text{P)}_3\] (X = Br or I) by boiling a benzene solution of \(\text{Ir}-\text{allyl nickel iodide or bromide with triphenylphosphine. Chatt and Booth (31) have obtained the nickel(II) complexes \[\text{NiX}_2\left(\text{Me}_2\text{P.C}_2\text{H}_4\text{PMe}_2\right)\] (X is Cl, Br or I) by reacting nickel(II) halides with the diphosphine in ethanol. The nickel(II) bromide complex \[\text{NiBr}_2\text{(diphos)}\] on oxidation with bromine, gave nickel(III) complex \[\text{NiBr}_3\text{(diphos)}\]. The four
oxidation states of cobalt have also been stabilized. Chatt and Watson (56) have prepared the zerovalent cobalt complex \( \text{[Co(diphos)\(_2\)]} \) (diphos is 1,2-bis(diphenyl phosphino)ethane) by reducing the corresponding dichloro complex with sodium naphthalenide in tetrahydrofuran. The cobalt (I) complexes \( \text{CoX(NO)}_2\text{PPh}_3 \), were obtained by Hieber and Heinecke (100,101) by the action of triphenyl phosphine on the corresponding dinitrosyl cobalt halide. The cobalt(II) complexes \( \text{[CoX}_2\text{(diphos)}] \) were obtained by Sacco and Gorieri (158) by reacting the respective cobalt(II)halide with 1,2-bis(diphenylphosphino)ethane in acetone. Vemanz and his coworkers (91) have reported the formation of octahedral diamagnetic complexes of cobalt(III) of the type \( \text{[CoX}_2(QP)]^+ \) where QP is tris(o-diphenylphosphino-phenyl)phosphine.

Role of tertiary phosphines in organic chemistry and industry

Many complexes of metal halides and metal carbonyls with phosphines have been used as catalysts in the cyclization of olefins, acetylene and their derivatives. Thus Rose and Statham (156) have reported the cyclisation of phenyl acetylene and phenyl ethynylcarbinol into 1,2,4-triphenyl benzene and 1,3,5-tri(\(\alpha\)-hydroxy benzyl)benzene respectively by using \( \text{[Ni(CO)}_2\text{(Ph}_3\text{P)}_2\] as catalyst. Bensen and Lindsey (16) have reported the cyclopolymerisation of allene into trimers 1,2,4- and 1,3,5-trimethylene cyclohexane and a stable tetramer 1,3,5,7-tetramethylene cyclooctane in the presence of
The ditertiary phosphines have been used as intermediates for the preparation of phosphorus containing heterocyclic compounds. Issleib and Krech (114) have reacted dillithium trimethylene-1,3-bis(phenylphosphide) with ethylene dibromide in benzene-tetrahydrofuran mixture to get 1,2-diphenyl-1,2-diphospha-cyclopentane

\[
\text{PhLiP(CH}_3\text{)}_2\text{PPh} + \text{C}_2\text{H}_4\text{B}_2\text{v} \rightarrow \text{H}_2\text{C} - \text{C}_2\text{H}_4\text{B}_2\text{v} + 2\text{LiB}_2 + \text{H}_2\text{C=CH}_2
\]

The phosphorane derivatives, prepared from tertiary phosphines, have been used in Wittig syntheses for the conversion of aldehydes and ketones into olefins. Thus Seyferth and his coworkers (168) have used triphenyl phosphine chloromethylene, prepared by adding n-butyl lithium in ether to triphenylphosphine and methylene dichloride in ether at -30°, for the conversion of acetophenone into 1-chloro-2-phenyl-1-propene and diethyl ketone into 1-chloro-2-ethyl-1-butene.

The tertiary phosphines act as catalysts in the esterification of salts of carboxylic acids with alkyl halides. Thus triphenyl phosphine catalyses the esterification of sodium acetate with benzyl chloride (193). Addition of triphenyl phosphine in ether to a solution of formaldehyde in
dimethyl ether at \(-101^\circ\) results in its polymerization to give a tough translucent film at 190-200\(^\circ\) (138).

Snyder (174) has used triphenyl phosphine as an auxiliary froth-floatation agent that is as an activator for the oxides and carbonates of manganese, zinc, and palladium etc. Some phosphines have also been used as anti-corrosion agents in steel. Thus Balezin and Ignat'eva (4) have found that the addition of triphenyl phosphine results in considerable decrease of the rate of solution of steel samples in hydrochloric acid or nitric acid.

**Nature of bonding in complexes of tertiary phosphines**

The tertiary phosphines with phosphorus as the donor atom belong to the \(\tilde{n}\)-acceptor group of ligands. This phosphorus atom in these ligands has vacant 3d orbitals in addition to the lone pair of electrons. These vacant 3d orbitals are capable of accepting electron density from filled non-bonding d orbitals of a transition metal ion to form a type of \(\tilde{n}\) bonding which supplements the \(\sigma\) bonding due to electron lone pair donation to the metal ion. Due to this ability to accept electron density into low lying empty orbitals these are also called \(\tilde{n}\)-acid ligands. Thus phosphines act as \(\sigma\)-bond donors and \(\tilde{n}\)-bond acceptors forming bonds to the metal using \(\sigma\)-orbitals and exercising their \(\tilde{n}\)-acidity using \(\tilde{n}\)-orbitals whose nodal planes include the axis of the \(\sigma\) bond. Sometimes
this \( \pi \) bonding becomes as important as the \( \sigma \) bonding in complex formation. Thus phosphorus trifluoride gives stable complexes with platinum(II)chloride where much reduced donor character is compensated by the increased electron affinity of the vacant 3d orbitals of the phosphorus atom because of the highly electronegative fluorine. Generally stable complexes are formed when the metal has its low energy d orbitals completely occupied by electrons and high energy orbitals vacant. The high ligand field strength of monotertiary and ditertiary phosphines ensures a large energy difference between the low energy and high energy d orbitals of the metal.

4-Methyl-o-phenylenebis(diethylphosphine) is probably the first ditertiary phosphine reported. At present nearly fifty alkylene and phenylene ditertiary phosphines are known of which 1,2-bis(diethyl phosphino)ethane and 1,2-bis (diphenyl phosphino)ethane have been most extensively employed for the study of their complexes with metal ions.

Complexes of ditertiary phosphines with transition metals:

Tuck and Carty (26) have isolated the tetra-coordinate indium(III) complex \([\text{In(DPE)}_2 (\text{ClO}_4)_3]\) by reacting 1,2-bis (diphenylphosphino)ethane with indium(III) perchlorate in methanol-carbon tetrachloride. They have also prepared
adducts of indium(III) bromide and iodide with this very diphosphine in ethyl acetate (27). The behaviour of these complexes indicates five coordination for indium. Carty (25) has isolated addition complexes of the type GaX2·0.5 Diphos. (X is Cl, Br or I) by reacting the corresponding anhydrous gallium(III)halide with diphosphine in benzene. The conductance data of these complexes support ionic structure (GaX2·DPE)(GaX4).

Chatt and Hayter (43) have obtained complexes of titanium (IV) chloride with ditertiary phosphines 1,2-bis(diethylphosphino)ethane, 1,2-bis(diphenylphosphino)ethane and o-phenylene-bis(diethylphosphine). All the complexes are of the type [TiCl4(diphos)] in which titanium has been presumed to be octahedrally coordinated. The reaction of titanium(IV) chloride and 1,2-bis(diphenylphosphino)ethane in dry benzene, in varying proportions of the reactants, yields three different complexes (DPE)2Ti3Cl12, DPE·TiCl4 and (DPE)3Ti2Cl8 (287). Beattie and Webster (9) have assigned cis structure to the complex (DPE)TiCl4 on the basis of the infra-red spectra. Nyholm and his coworkers (58) have obtained a 1:2 adduct of titanium(IV) chloride with o-phenylenebis(dimethylphosphine) while with o-phenylenebis(diethylphosphine) they have got only 1:1 adduct. It has been argued that the factor determining the coordination number of titanium is not the relative
donor property of phosphines but the steric and inductive properties of methyl as compared with the ethyl substituents on the donor atom. Westland and Ray (152) have prepared and studied the infra red spectra of the complexes of zirconium(IV) chloride, zirconium(IV) bromide and hafnium(IV) chloride with 1,2-bis(diphenylphosphino)ethane. Fowles and Walton (83) have reacted titanium(IV) and zirconium(IV) halides with the same diphosphine. With zirconium(IV) halides, no pure compound could be isolated but with titanium(IV) chloride they separated a pure complex [TiCl₄(DPE)]. In case of titanium(IV) bromide, it was practically reduced to titanium(III).

The reduction of a mixture of vanadium(III) chloride and 1,2-bis(dimethylphosphino)ethane with sodium naphthalenide has given the zerovalent vanadium complex [V(diphos)₃] (54,56). Walton and his coworkers (19) have attempted to prepare the vanadium(IV) chloride complex with 1,2-bis(diphenylphosphino)ethane in carbon tetrachloride but found that the reaction resulted in partial reduction of vanadium(IV) to vanadium(III).

Chatt and Watson (54,56) have isolated complexes of zerovalent chromium, molybdenum and tungsten with 1,2-bis(dimethylphosphino)ethane by reducing a mixture of metal chloride and the diphosphine in 1:3 ratio in dry tetrahydrofuran with sodium naphthalenide. Similar complexes of zerovalent molybdenum with the diphosphines
R₂P.C₂H₄.P₄₂ (R is CH₃ or C₆H₅) and o-C₆H₄(PEt₂)₂ have been prepared by them (53) by treating dibenzene molybdenum with the respective diphosphine in a sealed tube under nitrogen. Behrens and Mueller (13) have obtained the complex [Cr(DPE)₃] by the treatment of K₄[Cr(CN)₆] with 1,2-bis(diphenylphosphino)ethane in liquid ammonia.

The hexacarbonyls of chromium, molybdenum and tungsten (55) react with the diphosphines CH₂(PPh₂)₂, C₂H₄(P₂R₂)₂ and o-C₆H₄(PEt₂)₂ (R is Et or Ph) when two or four carbonyl groups are replaced depending upon the experimental conditions and the electronegativity of the diphosphine. While substituted chromium derivatives exhibited cis-trans isomerism, derivatives of molybdenum and tungsten exist only in the cis-form. Chatt and his coworkers (51,52) have obtained two types of dinuclear phosphorus bridged complexes by reacting the diphosphines R₂P.P₄₂ (R is alkyl or aryl group) with the carbonyls of chromium, molybdenum and tungsten. At higher temperature, complexes of the type [M₂(P₂R₂)₂(CO)₈] with metal in the monovalent state and bridging phosphide group have been obtained while under less drastic conditions, complexes of the type [M₂(diphos)(CO)₁₀] with zerovalent metal and bridging diphosphine have been obtained. Similar binuclear complexes [M₂(DPE)(CO)₁₀] (M is Mo or Cr) have been prepared by Werner and his coworkers (185) by treatment of metal hexacarbonyl with
the diphosphine in the molar ratio of 2:1 under very mild conditions. Further addition of the ligand leads to the formation of \([\text{M(diphos})(\text{CO})_4]\). The complex \([\text{Mo(CO)}_4\text{(Me}_2\text{P})]_2\) on irradiation with visible light in the presence of 1,2-bis(diphenylphosphino)ethane (DPE) gives the complex \([\text{Mo(Me}_2\text{P})(\text{CO})_3]_2\text{(DPE)}\) (178). Adams (1) has studied the infra-red spectra of the complexes \([\text{M(CO)}_4\text{(diphos)}]\) where \(\text{M}\) is Cr, Mo or W; diphos is \(\text{CH}_2\text{(PPh}_2)_2\), \(\text{C}_2\text{H}_4\text{(PR}_2)_2\) and \(\text{o-C}_6\text{H}_4\text{(PEt}_2)_2\) (\(\text{R}\) is Et or Ph). Lewis and Whyman (130) have prepared complexes of the type \([\text{M(CO)}_3\text{(DPE)}X_2]\) \(\text{M}\) is Mo, or W; and \(\text{X}\) is Br or I) by treatment of the corresponding metal tetracarbonyl diphosphine complex, \([\text{M(CO)}_4\text{(DPE)}]\), with two equivalents of bromine or iodine in methylene chloride. The bis-diphosphine complexes \([\text{M(CO)}_2\text{(diphos)}_2]\) on treatment with three equivalents of iodine gave stable paramagnetic complexes of the type \([\text{M(CO)}_2\text{(diphos)}_2]I_3\). These complexes were univalent electrolytes and isolation of the perchlorates \([\text{M(CO)}_2\text{(diphos)}_2]\text{ClO}_4\) confirmed their formulation as molybdenum-(I) and tungsten-(I) derivatives. Issleib and Biermann (108) have prepared complexes of the type \([\text{R}_2\text{PCH}_2\text{H}_4\text{PHR}_2]\text{[Mo(SCN)}_4\text{]}_2\text{[R}_2\text{PC}_2\text{H}_4\text{PR}_2]\) \(\text{R}\) is \(\text{C}_2\text{H}_5\) or \(\text{C}_6\text{H}_11\) and \([\text{R}_2\text{PCH}_2\text{H}_4\text{PHR}_2]\text{[Mo(SCN)}_4\text{]}_2\text{[R}_2\text{PC}_2\text{H}_4\text{PR}_2]\) \(\text{R}\) is \(\text{C}_6\text{H}_5\) by reacting 1,2-bis(diethylphosphino)ethane and 1,2-bis(diphenylphosphino)methane with \(\text{K}_3\text{[Mo(SCN)}_6]\).
Hieber and Freyer (99a) have prepared the complex $[\text{Mn}_2(\text{CO})_9(\text{Ph}_2\text{FCH}_2\text{PPh}_2)]$ by refluxing a mixture of manganese carbonyl and the diphosphine in dry xylene. Sacco (157) has reacted decacarbonyl dimanganese with 1,2-bis(diphenyl-phosphino)ethane in the ratio of 1:2 to isolate the complex $[\text{Mn}(\text{CO})_3(\text{DPE})]$. With excess of the ligand, he has isolated another complex $[\text{Mn}(\text{CO})_2(\text{DPE})_2][\text{Mn}(\text{CO})_5]$ which on treatment with chloroform gave the complex $[\text{Mn}(\text{CO})_2(\text{DPE})_2]\text{Cl}$. Stiddard and Osborne (148) have studied the action of DPE on bromo- and iodopentacarbonyl manganese and obtained the complexes $[\text{Mn}(\text{CO})_3(\text{DPE})\text{X}]$ (X is Br or I) which are octahedral, monomeric and non-electrolytes. With chloropentacarbonyl manganese, however, they (149) have isolated salt like complex $[\text{Mn}(\text{CO})_2(\text{DPE})_2]\text{Cl}$ which has trans disposition for carbonyl groups. This has been attributed to higher electronegativity of chlorine as compared with bromine and iodine. The analogous perchlorate has been prepared by ion exchange in methanol. Wojcicki and Farona (80) have treated the thiocyanatopentacarbonyl manganese with excess of diphosphine and isolated the complex $[\text{Mn}(\text{CO})_3(\text{DPE})\text{CNS}]$. Stiddard and Snow (173) have oxidised the complex $[\text{Mn}(\text{CO})_2(\text{DPE})_2]\text{Cl}$ with a number of oxidising agents leading to the formation of a green paramagnetic manganese(II) cation $[\text{Mn}(\text{CO})_2(\text{diphos})_2]^{2+}$ which has been isolated as the perchlorate. The two carbonyl groups have been assigned trans configuration on the basis of infra-red studies.
Haszeldine and coworkers (6) have reacted 1,2-bis (diphenylphosphino)ethane with phenyl manganese carbonyl when two carbonyl groups were replaced to give the complex PhMn(CO)$_3$(diphos)$_2$. Basolo and his coworkers (136) have studied the reaction of DPE with methyl manganese carbonyl and found that it first gives the stable intermediate $[\text{CH}_3\text{COMn(CO)}_4-(\text{DPE})]$ in which only one phosphorus atom of the ligand is attached to the metal atom. In a few days this intermediate changes into the chelate $[\text{CH}_3\text{COMn(CO)}_3(\text{DPE})]$. They have also prepared the complex $[\text{Mn(CO)}_3(\text{DPE})\text{Br}]$ with excess of the Grignard reagent $\text{C}_6\text{H}_5\text{CH}_2\text{MgCl}$. Hayter and Williams (98) have prepared binuclear complexes of the type $[\{\text{C}_5\text{H}_5\text{Mn(CO)}_2\}^2-(\text{diphos})]$ where diphos is $\text{CH}_2(\text{PPh}_2)_2$ or $\text{C}_6\text{H}_4(\text{PF}_2)_2$ and $R$ is Ph or Et, by the reaction of cyclopentadienyltricarbonyl-manganese with the respective diphosphine. By changing the concentration of reactants to equimolar ratio they have also obtained disubstituted complexes of the type $[\text{C}_5\text{H}_5\text{Mn(CO)}(\text{diphos})]$. Binuclear complexes have also been obtained with tetramethyl- and tetraphenyl diphosphines by them. Nyholm and coworkers (147, 129) have studied the reaction of 1,2-bis(diphenylphosphino)ethane on cyclohexadienyl tricarbonyl manganese and methylcyclopentadienyl tricarbonyl manganese under the influence of ultra violet light and have isolated complexes of the type $[\text{RMn(CO)}_2]^2$(diphos) and $[\text{RMn(CO)}$(diphos)] where $R$ is cyclopentadienyl or methylcyclopentadienyl.
Chatt and Howe (46) have reported the formation of rhenium(V) complex [ReOCl₃(DPE)]. By using a higher molar proportion of the diphosphine, they have obtained the rhenium(III) complex [ReCl₂(DPE)₂]Cl which, on reduction with sodium borohydride, gave the rhenium(II) complex [ReCl₂(DPE)₂]. Cotton and his coworkers (62) have reacted octahalodirhenium(III) ion with 1,2-bis(diphenylphosphino)ethane and have obtained three types of complexes viz. [Re(DPE)Cl₃]ₙ which is five coordinate monomer or a chlorine bridged dimer; [Re(DPE)X₂] Y (X is Cl or Br; Y is X or ClO₄) which are six coordinate mononuclear rhenium(III) complexes and finally the trans-dioxorhenium(V) complex [Re(DPE)O₂]ClO₄. Cotton and Walton (65) treated rhenium(III) chloride with the same diphosphine DPE in tetrahydrofuran to isolate the red complex [Re₃Cl₉(DPE)₁₋₅] which is believed to have the bridging bidentate ligand. Chatt and Coffey (32) have prepared and characterised the rhenium hydride complex [ReH₇(DPE)].

Giusto and his coworkers (85) have treated iodopenta-carbonyl rhenium with DPE to obtain the complex cis-[Re(CO)₃(DPE)] which, on treatment with more of ligand, gives the uni-univalent salt [Re(CO)₂(DPE)]I in which the iodide ion can be replaced by chloride, perchlorate, nitrate tetraphenylborate and trichlorostannite. These salts [Re(CO)₂(DPE)] X (X is Cl', Br' or SnCl₃') on heating in sealed tubes at 270° give diamagnetic non-electrolytes.
[Re(CO)(DPE)₂]⁺. Giusto and his coworkers (34) have studied the reaction of DPE on decacarbonyl dirhenium in sealed tubes at high temperature and have prepared complexes of the type cis[Re(CO)₃(DPE)], trans [Re(CO)₃(DPE)], cis-[Re(CO)₂(DPE)₂] and [Re(CO)(DPE)₂] which, on reaction with iodine, give trans [Re(CO)₃(DPE)]I, cis [Re(CO)₂(DPE)₂I₃] and finally [Re(CO)(DPE)₂]I.

Chatt and his coworkers (35,42,45) have reported iron(II) and iron(III) complexes of the type trans [FeCl₂(diphos)₂] and [FeCl₂(diphos)₂][FeCl₄] (diphos is C₂H₄(PR₂)₂ and o-C₆H₄(PEt₂)₂; R is Me or Et). On reduction with lithium aluminium hydride, these complexes give monohydrides [FeHCl(diphos)₂] and a dihydride [FeH₂{ o-C₆H₄(PEt₂)₂}]₂⁺. This dihydride complex has also been obtained by dissolving finely divided iron in the diphosphine at 120°C under hydrogen. On treatment with one equivalent of hydrogen chloride in dry ether, it gives trans [FeHCl(diphos)₂]⁺. Chatt and Watson (56) have prepared the four coordinate planar iron(0) complex [Fe(C₆H₄Me₂P₂CH₂PMe₂)₂] by the reduction of the complex trans-[FeCl₂(diphos)₂] with sodium naphthalenide in dry tetrahydrofuran. Iron(II) bromide reacts with 1,3-bis(dicyclohexylphosphino)propane and 1,5-bis(dicyclohexylphosphino)pentane in isopropanol to give the complexes [FeBr₂{Re₄P(CH₂)nPR₂}] R is C₆H₁₁ and n is 3 and 5 (113).
Iron carbonyl complexes of the type \([\text{Fe(CO)}_3\text{DPE}]\) have been reported in literature (196). Reckziegel and Bigorgne (153) have prepared and studied the infrared spectra of the complexes \([\text{Fe(CO)}_4\text{(DPE)}]\) and cis \([\text{Fe(CO)}_3\text{(DPE)}_2]\). Chatt and Thornton (32) have studied the reaction of tetramethyl- and tetraethyl diphosphines on iron pentacarbonyl and have isolated the phosphido bridged complexes \([\text{Fe}_2(\text{PR}_2)_2(\text{CO})_6]\) (R is Me or Et) as well as the diphosphine bridged complex \([\text{Fe}_2(\text{CO})_8(\text{P}_2\text{Me}_4)]\).

The structure of these two types of complexes has been discussed on the basis of dipole moment and infrared spectral measurements. Thompson (176), on irradiation of the complex bis(n-dimethylphosphido)-bis(tricarbonyl iron) in the presence of 1,2-bis(diphenylphosphino)ethane, has obtained two products. In one of these, the two carbonyl groups of the complex are replaced by the diphosphine while in the other, one carbonyl group from each of the two molecules of the complex is replaced by the diphosphine to give a compound having four metal atoms in which two dinuclear fragments are linked by a diphosphine. Manuel (134) has prepared the dichloro dicarbonyl (diphosphine) iron(II) i.e. \([\text{FeCl}_2(\text{CO})_2(\text{DPE})]\) by refluxing a mixture of ferric chloride and 1,2-bis(diphenylphosphino)ethane in benzene followed by its stirring under carbon monoxide pressure.

Hieber and Neumair (103) have prepared the complex \([(\text{NO})_2\text{Fe(Ph}_2\text{P})_2]\) by treating dinitrosyl iron halides with potassium diphenyl phosphide. On reacting these nitrosyl iron
halides with 1,2-bis(diphenylphosphino)ethane, they have isolated both monomeric complexes with five membered rings as well as binuclear \( \mu \)-phosphino complexes with diphosphine chain. Using tetraphenyldiphosphine as the ligand, Hieber and Kummer (102) have obtained the complexes \([(NO)_2Fe(R_2PPR_2)]\) and the binuclear phosphido bridged complexes \([X(NO)_2Fe(PR_2)]_2\) and \([(NO)_2Fe(PR_2)]_2\) (\(R\) is \(C_6H_5\) and \(X\) is halogen).

Basolo and his coworkers (136) have treated \(Fe(NO)_2(CO)_2\) with excess of 1,2-bis(diphenylphosphino)ethane to get \([Fe(NO)_2(diphos)]\) through the formation of a fairly long lived intermediate \([Fe(NO)_2(CO)(diphos)]\) in which the diphosphine is attached to the metal atom only through one phosphorus atom.

Chatt and Hayter (40) have reported ruthenium(II) and osmium(II) complexes of the general type cis- and trans- \([MCl_2(diphos)]\) where diphos is \(C_2H_4(PR_2)_2\), \(CH_2(PPh_2)_2\) and \(o-C_6H_4(PEt_2)_2\) (where \(R\) is Me, Et or Ph). The complexes with trans configuration have been prepared by refluxing a mixture of diphosphine and \(RuCl_3\) or \((NH_4)_2OsCl_6\) in aqueous ethanol, while those of cis type have been obtained by the reaction of the diphosphine with the monotertiary phosphine complexes like \([M_2Cl_3(PR_3)_2]Cl\). Other cis and trans complexes of the type \([MX_2(diphos)]\) (\(X\) is \(Br\), I, SCN, CN or OAc) have been prepared from the corresponding cis or trans dichloro complex by reaction with the appropriate metal salt. Chatt and his coworkers (45)
have also prepared \( \text{cis}[\text{C}_2\text{H}_4(\text{PEt}_2)_2]\text{RuCl}_2, \text{cis}[\text{C}_2\text{H}_4(\text{PMes}_2)_2]\text{RuCl}_2, \)
\( \text{cis} \) and \( \text{trans} \) \( \text{cis}[\text{C}_2\text{H}_4(\text{PPh}_2)_2]\text{OsCl}_2 \) and \( \text{cis}[\text{C}_2\text{H}_4(\text{PPh}_2)_2]_2\text{OsCl}_2 \) by heating \( [(\text{PPhEt}_2)_3\text{MCl}_2]_2 \) (\( \text{M} \) is Os or Ru) with the corresponding ditertiary phosphine under nitrogen.

Chatt and his coworkers \((41,39,45)\) have obtained ruthenium and osmium hydrido complexes of the type \( \text{trans} [\text{MHX}(\text{diphos})_2] \)
(\( \text{M} \) is Os, or Ru; \( \text{X} \) is Cl, Br or I; \( \text{diphos} \) is \( \text{C}_2\text{H}_4(\text{PR}_2)_2 \), \( \text{CH}_2(\text{PPh}_2)_2 \) or \( \text{o-C}_6\text{H}_4(\text{PEt}_2)_2, \text{R} \) is \( \text{CH}_3 \) or \( \text{C}_2\text{H}_5 \)) by the reduction of the corresponding dihalogen complexes \( \text{cis}[\text{MX}_2(\text{diphos})_2] \) with lithium aluminium hydride. In case of the complexes \( \text{trans}[\text{RuHCl}(\text{C}_2\text{H}_4(\text{PR}_2)_2)_2] \) (\( \text{R} \) is \( \text{CH}_3 \) or \( \text{C}_2\text{H}_5 \)) the chloride has been replaced by thiocyanate, cyanide or nitrite anion by treatment with corresponding alkali metal salt, as well as by hydrogen, on treatment with excess of lithium aluminium hydride.

The alkyl and aryl derivatives of ruthenium and osmium of the type \( \text{cis}[\text{MR}_2(\text{diphos})_2] \) and \( \text{cis} \) and \( \text{trans} \) \( \text{cis}[\text{MXR}(\text{diphos})_2] \)
(\( \text{M} \) is Os or Ru; \( \text{X} \) is Cl, Br or I; \( \text{R} \) is alkyl or aryl group; \( \text{diphos} \) is \( \text{C}_2\text{H}_4(\text{PR}_2)_2 \), \( \text{CH}_2(\text{PPh}_2)_2 \) (\( \text{R} \) is \( \text{CH}_3 \) or \( \text{C}_6\text{H}_5 \)) have been obtained by Chatt and Hayter \((44)\) by reacting the corresponding dihalogeno complex with alkyl or aryl-lithium or trialkyl-aluminium. On treatment with lithium aluminium hydride, the halogeno alkyl and aryl derivatives give the corresponding hydrido-alkyl or aryl complex.

Rhodium carbonyl chloride, on treatment with 1,2-bis (diphenylphosphino)ethane (DPE) in benzene, has given the
rhodium(I) complex \([\text{Rh}(\text{DPE})_2] \text{Cl}\) (161). The corresponding perchlorate and tetraphenylborate complexes have been obtained by anion exchange in alcoholic solution. With lithium aluminium hydride in tetrahydrofuran, this chloro complex gives a very stable hydride complex of rhodium(I) \([\text{RhH}(\text{DPE})_2] \) . Both the chloro complex \([\text{Rh}(\text{diphos})_2] \text{Cl}\) as well as the hydrido complex \([\text{RhH}(\text{DPE})_2] \), on treatment with hydrogen chloride give a hydrido complex of rhodium(III) \([\text{RhHCl}(\text{DPE})_2]\text{Cl}\) . Chatt and Shaw (50) have obtained rhodium(I) complex \([\text{Rh}(\text{DPE})_2] \text{Cl}\) by the reaction of diphosphine with trans-\([\text{RhCl}(\text{CO})(\text{PET}_2\text{Ph})_2]\). Chatt and coworkers (45) have prepared another hydrido complex \([\text{Rh}_2\text{H}_2\left\{\text{O-C}_6\text{H}_4(\text{PET}_2\text{Ph})_2\right\}_3]\) by heating a mixture of the diphosphine and rhodium black under hydrogen at 200° for 17 hours.

The irridium complex \([\text{IrCl}(\text{CO})(\text{DPE})_2]\text{Cl}\) has been prepared by Sacco and his coworkers (160) by treating the complex \([\text{IrCl}(\text{CO})(\text{o-toluidine})] \text{or } [\text{IrCl}(\text{CO})(\text{PPh}_3)_2]\) with 1,2-bis(diphenylphosphino)ethane in benzene. The corresponding complexes \([\text{IrCl}(\text{CO})(\text{DPE})_2] X (X \text{ is } \text{Br, I, ClO}_4 \text{ or } \text{BPh}_4)\) have been obtained by anion exchange from the chloro complex. Hieber and Frey (99) have treated the irridium complex \([\text{IrCl}(\text{CO})_2(\text{o-toluidine})]\) with the same diphosphine and have got the pentacoordinate complex ion \([\text{Ir}(\text{CO})(\text{DPE})_2]^+\) and the tetracoordinate complex \([\text{Ir}(\text{DPE})_2]\text{Cl}\).

The palladium(II) complex \([\text{Pd}(\text{diphos})\text{Br}_2]\) has been isolated by Mann and Hart (90) by treating an aqueous ethanolic solution of potassium tetrabromopalladate(II) with
4-methyl-o-phenylenebis(diethylphosphine). Mann and Hinton (305) have also prepared two types of 4-coordinate palladium(II) complexes, \([\text{Pd(diphos)Br}_2]\) and \([\text{Pd(diphos)}_2]\) \(\text{(PdBr}_4\) where diphos is 1,4-dibenzyl- and 1,4-diphenyl diethylenediphosphine). Bailar and Wymore (291) have isolated the complex \([\text{Pd(diphos)Cl}_2]\) by reacting ammonium tetrachloro-palladate with 1,2-bis(diethylphosphino)ethane. The preparation of similar complexes \([\text{Pd(diphos)Cl}_2]\) where diphos is tetraphenyl- and tetracyclohexyl diphosphine, has been reported by Issleib and Schwager (115,116). Chatt and his coworkers (38) have reported a number of palladium(II) complexes of the type \([\text{Pd(diphos)}_2]X_2\) \((X \text{ is Br or NO}_3\); diphos is \(\text{C}_6\text{H}_4(\text{PET})_2\), \(\text{C}_2\text{H}_4(\text{PR})_2\) and \(\text{CH}_2(\text{PPh})_2\) where \(R \text{ is C}_6\text{H}_5 \text{ or C}_2\text{H}_5\)). On reduction with an appropriate reducing agent, these palladium(II) complexes give the corresponding palladium(0) complexes of the type \([\text{Pd(diphos)}_2]\). When this reduction of palladium(II) complexes was carried out in the presence of equimolar ratio of another ditertiary phosphine, they isolated unsymmetrical palladium(0) complexes of the type \([\text{Pd(diphos)(diphos')}\]). The palladium(0) complex \([\text{Pd}\{\text{o-C}_6\text{H}_4(\text{PET})_2\}_2]\) has also been prepared by reacting the diphosphine directly with finely divided palladium metal (36). Westland (186) has prepared palladium(II) and platinum(II) complexes of the composition \([\text{M(DPE)}_2]X_2\) \((\text{M is Pd or Pt; X is Cl,Br, I or NO}_3, \text{ClO}_4\)). Molar conductivities and conductometric titrations in nitromethane have shown the presence of five coordinate species \([\text{MX(diphos)}_2]\)^+. Bailar and Wymore (191) have reported the complexes of copper(I) and silver(I) iodide with 1,2-bis(diethylphosphino)ethane
which have been, on the basis of their conductivity in nitrobenzene, assigned the formulae \([\text{Cu}(\text{diphos})_2]([\text{Cu}(\text{diphos})X)_2]\) and \([\text{Ag}(\text{diphos})_2][\text{Ag}X_2]\). Seidel (165, 166, 167) has prepared copper(I) and silver(I) complexes with dipiperidino dicyclohexyl diphosphine, dipiperidinodiphenyl diphosphine and piperidinetricyclohexyl diphosphine in which these diphosphines act as bidentate ligands giving complexes of the type \([(\text{diphos})_2\text{MX}].\)

Naldini and Cariati (140) have obtained complexes of the type \([\text{CuX}((\text{DPE})_3 (X \text{ is } \text{Cl or Br}};\text{DPE is } 1,2\text{-bis(diphenylphosphino)ethane})\) by refluxing a suspension of copper(I) halide and the ligand in chloroform. Complexes of the type \([(C_6H_{11})_2PF(CH_2)_3P(C_6H_{11})_2Cu_2Br_2]\) and \([(C_6H_{11})_2PF(CH_2)_3P(C_6H_{11})_2Cu_2Br]\) have been reported by Issleib and Hohlfeld (113).

Mann and Hart (90) have reported the preparation of four coordinate complexes of gold(I) with 4-methyl-o-phenylenebis(diethylphosphine) with the formula \([\text{Au}(\text{diphos})_2X].\) With the ligand 1,2-bis(diethylphosphino)ethane, gold(I) iodide gave the complex \(\text{IAu}(\text{diphos})\text{AuI}\) in which gold was probably linear 2-coordinate (191). A similar complex \(\text{IAu}(\text{diphos})\text{AuI}\) has been characterized by Mann and Hinton (105) using triethylene diphosphine as the ligand. Venanzi and Chiswell (182) have reported the preparation of the bidentate ligand diphenyl-3,3'-bis diphenylphosphine and its gold(I) chloride complex \(\text{ClAu}(\text{diphos})\text{AuCl}\). Mann and Davis (69) have employed the unsymmetrically substituted diphosphines 4-methyl-o-phenylenebis
(diethylphosphine), biphenylene-3,4-bis(diethylphosphine) and o-diethylphosphinophenyl diphenyl phosphine to prepare complexes with gold(I) iodide. All the complexes, in the crystalline state, have got a tetrahedral bis(diphosphine)gold(I) cation. With (2-diethylphosphino-5-methyl benzyl)diethylphosphine, they could get only 3-coordinate gold derivative. They have also prepared and studied gold(III) complexes with o-phenylene-bis(diethylphosphine).

Complexes of tritertiary phosphines with transition metals

Chatt and Watson (55) have studied the action of tritertiary phosphines PhP(C₆H₄PEt₂)₂ and PhP(C₂H₄PPh₂)₂ and MeC(CH₂PPh₂)₃ on the hexacarbonyls of chromium, molybdenum and tungsten and have found that only three carbonyl groups are replaced by the ligand and further replacement does not occur even in the presence of excess of ligand and high temperature. With the tritertiary phosphine 1,1,1, tris(diphenylphosphinomethyl)ethane, Chatt and coworkers (38) have obtained nickel(0) and palladium(0) complexes of the type \([\text{M(triphos)}₂]\) by the reduction of the corresponding nickel(II) and palladium(II) complex in the presence of free ligand with sodium borohydride. These complexes have exhibited a novel type of isomerism between an octahedrally coordinated form and a form of lower coordination number. When the diphosphine complex \([\text{PdCl₂(o-C₆H₄(PEt₂)₂)}]\) was reduced with sodium...
borohydride in the presence of this triphosphine, they got an unsymmetrical palladium(η) complex

\[ \text{Pd}\{\text{o-C}_6\text{H}_4(\text{PET}_{2})_2\}\{\text{Me.C(CH}_2\text{PPh}_2)_3\} \]

in which palladium was thought to be five coordinate. With the triphosphine, phenylbis(o-diethylphosphinophenyl)phosphine, they have prepared the four coordinate palladium(II) complex

\[ \text{PdClPhP(o-C}_6\text{H}_4\text{PET}_{2})_2\text{Cl} \]

Venanzi and his coworkers (92) have reported similar four coordinate palladium(II) and platinum(II) complexes \([\text{Ml(triphos)}] \text{I} \) and \([\text{Ml(triphos)}] \text{ClO}_4 \)

with the triphosphine, bis(o-diphenylphosphinophenyl)phenyl phosphine.

Complexes of tetradequate phosphines with transition metals

Venanzi and Chiswell (57) have reacted the quadridentate phosphine tris(o-diphenylphosphinophenyl) phosphine (\(\text{QP}\)) with the chloro- and bromopentacarbonyl manganese and have obtained three types of manganese(I) complexes in which this phosphine acts as bidentate \([\text{MnX(CO)}_3(\text{QP})]\), tridentate \([\text{Mn(CO)}_3(\text{QP})]^+\), and as tetradequate \([\text{Mn(CO)}_2(\text{QP})]^+\) ligand. That the phosphine behaves as bidentate and tridentate ligand in the first and second type of complexes is proved by the similarity of the infrared spectra of these complexes with those of the complexes formed by the bidentate ligand o-phenylenebis (diphenylphosphine) and tridentate ligand bis(o-diphenylphosphinophenyl)phenylphosphine with the respective halogeno
pentacarbonyl manganese. Using this very tetradentate phosphine, Venanzi and coworkers (92) have prepared six coordinate ruthenium(II) and osmium(II) complexes of the type \([M(QP)Cl_2]\). Venanzi and his coworkers (92) have also reported the formation of five coordinate trigonal bipyramidal palladium(II) and platinum(II) complexes of the type \([MX(QP)]X'\) (where \(M\) is Pd or Pt and \(X\) is \(X',I,Cl\), and \(X'\) is \(\text{BPh}_4\)).

Complexes of cyclic phosphines with transition metals

West and Ang (2) have treated the hexacarboxyls of chromium, molybdenum and tungsten with the cyclic phosphines \((PR)_5\) (\(R\) is Ph, Et or Me) to get complexes of the general formula \([(PR)_5\text{Mn(CO)}_n]\) (\(n\) is 5, 4 or 3). These are mononuclear complexes in which one, two or three carbonyl groups are displaced by the coordination of a single molecule of the cyclic phosphine which, thus, acts as a uni-, bi- and tridentate ligand. They have also studied the reaction of cyclic phosphines \((PR)_n\) (where for \(n = 5\), \(R\) is Ph or Me; and for \(n = 4\), \(R\) is Ph or Et) and have obtained the complexes, \([\{(\text{Fe(CO)})_3\}_2(PR)_4]\) with the phosphine \((PR)_4\). However, they have also obtained the complexes of the same type with \((PR)_5\) (where \(R\) is Ph or Me). With tetracarbonyl nickel(0), tetracyclic phosphine \((\text{PhP})_4\) behaves as a monodentate ligand giving a complex of the type \([(\text{PhP})_4\text{Ni(CO)}_3]\).
Complexes of bidentate mixed ligands containing phosphorus as one of the donor atoms

Mann and his coworkers (60) have employed mixed bidentate ligand having arsenic and phosphorus as donor atoms, o-diethylarsinophenyl diethylphosphine to react with copper(I), silver(I) and gold(I) halides to yield four coordinate complexes of the type \([\text{Cu(ligand)\textsubscript{2}}]\text{X}\) (\(X\) is Cl, Br or I), \([\text{Cu(ligand)\textsubscript{2}}][\text{CuX}\textsubscript{2}]\) (\(X\) is Cl or Br), \([\text{Ag(ligand)\textsubscript{2}}]\text{X}\) (\(X\) is I, AgCl\textsubscript{2} and AgI\textsubscript{2}) and \([\text{Au(ligand)\textsubscript{2}}]\text{X}\) (\(X\) is Cl or I). The X-ray examination of the complexes \([\text{M(ligand)\textsubscript{2}}]\text{I}\) (\(M\) is Cu or Au) shows them to be tetrahedrally coordinated. Mann and Jones (124) have obtained four coordinate palladium(II) complexes of the type \([\text{Pd(ligand)Br}\textsubscript{2}]\) and \([\text{Pd(ligand)\textsubscript{2}}]\text{Br}_\text{2}\) where the ligand is dimethyl(o-diethylphosphinophenyl)arsine. Meek and Nicpon (143) have also used the mixed arsenic-phosphorus bidentate ligand diphenyl(o-diphenyl arsinophenyl)phosphine to prepare four coordinate palladium(II) and platinum(II) complexes \([\text{M(chel)X}\textsubscript{2}]\) (\(M\) is Pd and \(X\) is Cl, Br, I or SCN; when \(M\) is Pt, \(X\) is Cl) and \([\text{Pd(chel)\textsubscript{2}}]\text{NO}_\text{3}\textsubscript{2}\text{. In case of palladium(II) thiocyanate, they have isolated two isomers viz.}\) \([\text{Pd(ligand)\textsubscript{2}}][\text{Pd(SCN)}\textsubscript{4}]\) and \([\text{Pd(ligand)(SCN)(NCS)}]\). The latter complex is unusual in the respect that it contains one nitrogen bonded and one sulphur-bonded thiocyanate ion in the same molecule.
Walsh and coworkers (72) have reacted the mixed nitrogen-phosphorus ligand \( \text{Ph}_2\text{PC}_{2}\text{H}_4\text{NET}_2 \) with hexacarbonyl molybdenum(0) to get the complex \([\text{Mo(ligand)(CO)}_4]\). The mixed ligand o-dimethylaminophenyldiethylphosphine has been used by Mann and Watson (133) to isolate palladium(II) complexes of the type \([\text{Pd(ligand)}X_2]\) (\(X = \text{Cl, Br, I or NO}_2\)), \([\text{Pd(ligand)}_2X_2\cdot 2\text{H}_2\text{O}\) (\(X = \text{Cl, Br or picrate}\)), \([\text{Pd(ligand)}_2X]X\) (\(X = \text{I or SCN}\)) and \([\text{Pd(ligand)}]_2\). Various coordination numbers other than four for palladium in complexes of the second, third and fourth type have been discussed. Venanzi and coworkers (85) have also reported the preparation of mixed ligand \((\text{o-Me}_2\text{N.C}_6\text{H}_4)\text{PPh}_2\) and its palladium(II) and platinum(II) complexes \([\text{M(ligand)}X_2]\) (\(M = \text{Pd or Pt; X is Cl, Br or I}\)).

Meek and coworkers (78) have used the mixed ligand diphenyl(o-methylthiophenyl)phosphine to get four coordinated planar palladium(II) complexes \([\text{Pd(ligand)}\text{Cl}_2]\) and \([\text{Pd(ligand)}_2](\text{ClO}_4)_2\).

**Complexes of tri- and tetradeutate mixed ligands containing one or more phosphorus donor atoms**

Walsh and his coworkers (72) have prepared and reacted the mixed nitrogen-phosphorus tritertiary ligands \(\text{PhP(CH}_2\text{CH}_2\text{NET}_2)_2\) and \((\text{PhPCH}_2\text{CH}_2)_2\text{NET}\) with hexacarbonyl molybdenum(0) to isolate the complexes \([\text{Mo(ligand)(CO)}_4]\) and
In the case of the second ligand all the three donor atoms get coordinated to molybdenum thus replacing three carbonyl groups. However, in the case of first ligand, only one of the two nitrogen atoms, in addition to the phosphorus atom, gets coordinated to the metal. This failure of the second nitrogen atom is attributed to the steric effects of ethyl groups. Similar results have been observed by Vananzi and his coworkers (86) with the mixed ligands (o-Me₂NC₆H₄)₂PPh and (oMe₂NC₆H₄)₃P which gave palladium(II) and platinum(II) complexes of the type [M(ligand)X₂] (M is Pd or Pt; X is Cl, Br or I). In both the cases, only the phosphorus atom and one of the nitrogen atoms are bonded to the metal.

Meek and coworkers (78) have studied the formation of palladium(II) complexes with the mixed sulphur-phosphorus tridentate ligand bis(o-methylthiophenyl)phenylphosphine(DSP) and the quadridentate ligand tris(o-methylthiophenyl)phosphine (TSP). The tridentate ligand (DSP) acts as a bidentate ligand in [Pd(DSP)Cl₂] but as a tridentate ligand in [Pd(DSP)Cl]ClO₄. Similarly quadridentate ligand TSP behaves as bidentate ligand in the complex [Pd(TSP)Cl₂] but as quadridentate ligand in the complex [Pd₂(TSP)Cl₄] by coordinating to two different palladium atoms.